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Katia [BR/BR]; Rua Guido Zecca, 38, Esplanada do Sol,
CEP-12244-680 São José dos Campos, SP (BR). SOUSA
SALES, Henrique, Jorge [BR/BR]; Avenida Dr. João
Batista de Queiroz Jr., 2361, Apto. 74, Jardim das Indús-
trias, CEP-12240-000 São José dos Campos, SP (BR).

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(74) Agent: **DANNEMANN, SIEMSEN, BIGLER &
IPANEMA MOREIRA**; Caixa Postal 2142, Rua Marquês
de Olinda, 70, CEP-22251-040 Rio de Janeiro, RJ (BR).

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(71) Applicant (*for all designated States except US*): **COGNIS
BRASIL LTDA.** [BR/BR]; Avenue das Nações Unidas,
10989-4° andar, CEP-04578-000 São Paulo, SP (BR).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BUENO DE
ALMEIDA, Wanderson** [BR/BR]; Rua República
do Libano, 314, Apto. 22, Jardim Osvaldo Cruz,
CEP-12216-590 São José dos Campos, SP (BR). **BRAGA,**

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: PLASTICIZER COMPOSITIONS FOR NITROCELLULOSE BASED RESINS

(57) Abstract: The invention relates to plasticizer compositions for nitrocellulose based resins comprising (a) 100 parts by weight of at least one nitro-cellulose resin and (b) 0,1 to 30 parts by weight of a plasticizer compounded with said at least one nitrocellulose resin. Said plasticizer comprises (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

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Title: **"Plasticizer compositions for nitrocellulose based resins"**

Field of the Invention

The invention relates to plasticizer compositions for nitrocellulose based resins.

Description of the Related Art

Paints or pigment concentrates based on nitrocellulose based resins are widely used for graphic arts and several industrial coatings. The most important property achieved with systems based on nitrocellulose is short drying time.

It is well known that nitrocellulose based resins are not flexible and must be plasticized before applying. Besides that application systems like paints and pigment concentrates must show a viscosity which is low enough so that the system is pumpable. Phthalic ester type plasticizers are commonly used in these systems, but they have been criticized because of their environmentally harmful action.

Detailed Description of the Invention

It was an object of the present invention to provide plasticizer compositions for nitrocellulose based resins, which overcome the difficulties and disadvantages of the prior art. It was a further object of the invention that paint formulations comprising those plasticizer compositions show a reduced viscosity compared with formulations based on phthalic acid esters like dioctyl phthalate (DOP). Within the present application the term "nitrocellulose based resins" means resins which comprise nitrocellulose. As it is known to the artisan nitrocellulose is nitrated cellulose.

According to the invention this is achieved by **plasticizer compositions** for nitrocellulose based resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids

can be saturated or olefinically unsaturated, linear or branched.

Preferably these plasticizer compositions are free of phthalic ester type plasticizers and especially free of dioctylphthalate.

In one embodiment the plasticizer compositions of the invention
5 contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. In another embodiment these plasticizer compositions contain exclusively compounds (i) and (ii).

The invention also relates to the use of compositions comprising
10 (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear
15 or branched **as plasticizers for nitrocellulose based resins**. As stated above the compositions are preferably free of phthalic ester type plasticizers.

As also stated above the compositions preferably contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35
20 and 55 : 45. Those plasticizer compositions which exclusively contain compounds (i) and (ii) are preferred.

The invention also relates to **nitrocellulose based paints** comprising (a) 100 parts by weight of at least one nitrocellulose resin , (b) 100 to 200 parts by weight of an alkyd resin and (c) 0,1 to 30 parts of a plasticizer
25 composition comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or ole-
30 finically unsaturated, linear or branched. Those nitrocellulose based paints which are free of phthalic ester type plasticizers are preferred.

As already stated above the plasticizer compositions contain

compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. Those plasticizer compositions which contain exclusively compounds (i) and (ii) are preferred.

5 The term "alkyd resins" is known to the artisan. All types of alkyd resins which are known to the artisan and especially all kinds of alkyd resins which are commercially available can be used within the context of the present invention.

10 All types of nitrocellulose based resins which are known to the artisan can be used within the context of the present invention, especially all kinds of nitrocellulose based resins which are commercially available.

Examples

IES = Isobutyl epoxy stearate.

15 **IFAME** = Mixture of methyl esters of fatty acids. The distribution of the fatty acid individuals in these methyl esters was (% means mole-%): straight chain C12 = 0.3%, branched chain C14 = 0.4%, straight chain C14 = 1.0%, branched chain C16 = 3.7% , straight chain C16 = 4.9%, branched chain C18 = 61.4%, straight chain C18 = 4.6%, cyclic C18 = 17.5%, straight chain C20 = 0.1%, aromatic C18 = 6.1%.

20 **NC ½** = Cellulose nitrate (Nitrocellulose 1/2 commercially available from Nitro Química).

Resanol 15-075 = pure coconut alkyd resin with 60% solid content and 40% xylene as solvent ("Resanol 15-075" commercially available from RESANA Química, Brasil); % means weight percent.

25 **Mix of solvents** = Mixture of 20% ethyl acetate, 17,5% butyl acetate, 12,5% butanol, 10% ethanol and 40% xylene (% means volume percent).

DOP = dioctyl phthalate

Example 1

30 (Nitrocellulose based paint)

The following compounds were mixed together in a vessel:

Mix of Solvents	278 g
Resanol 15-075	200 g
IES	15 g
IFAME	10 g

5 Under stirring it was added under nitrogen:

NC ½	100 g
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The resulting mixture (paint) was then homogenized and the viscosity of the system was measured. It was 3700 mPas. The value of the viscosity is lower compared to the formulation of comparative example 1 which is based on dioctyl phthalate as plasticizer.

Comparative Example 1

(Nitrocellulose based paint)

The following compounds were mixed together in a vessel:

Mix of Solvents	278 g
15 Resanol 15-075	200 g
DOP	25 g

Under stirring it was added under nitrogen:

NC ½	100 g
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20 The resulting mixture (paint) was then homogenized and the viscosity of the system was measured. It was 4200 mPas.

Claims

1. Plasticizer compositions for nitrocellulose based resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated,
5 linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

2. Compositions according to claim 1 with the proviso that the
10 compositions are free of phthalic ester type plasticizers.

3. Compositions according to claim 1 or 2 with the proviso that the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

4. Compositions according to claim 1 with the further proviso that
15 the compositions contain exclusively compounds (i) and (ii).

5. The use of compositions comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of
20 fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched as plasticizers for nitrocellulose based resins.

6. The use according to claim 5 with the proviso that the compositions are free of phthalic ester type plasticizers.

25 7. The use according to claim 5 or 6 with the proviso that the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

8. The use according to claim 5 with the further proviso that the compositions contain exclusively compounds (i) and (ii).

9. Nitrocellulose based paints comprising (a) 100 parts by weight
30 of at least one nitrocellulose resin, (b) 100 to 200 parts by weight of an alkyd resin and (c) 0,1 to 30 parts of a plasticizer composition comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that

the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

5 10. Nitrocellulose based paints according to claim 9 with the proviso that these paints are free of phthalic ester type plasticizers.

10 11. Nitrocellulose based paints according to claim 9 with the proviso that the plasticizer compositions contain exclusively compounds (i) and (ii).

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/04 C08L1/18 //(C08K5/04,5:1515,5:101)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 934 689 A (SWIFT & CO) 21 August 1963 (1963-08-21) claims 1,8 examples IV-VI ---	1-11
A	US 2 964 484 A (OHLSON JOHN L ET AL) 13 December 1960 (1960-12-13) examples ---	1-11
A	EP 0 337 237 A (NEYNABER CHEMIE GMBH) 18 October 1989 (1989-10-18) claims 1,2 ---	1-11
A	DE 38 39 418 A (CIBA GEIGY AG) 8 June 1989 (1989-06-08) claims 1,11,13 ---	1-11
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rose, E

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 1 538 861 A (LINDSAY WILLIAM G) 19 May 1925 (1925-05-19) claims 1,3 ---	1-11
A	US 1 357 876 A (KESSLER JOHANNES M) 2 November 1920 (1920-11-02) claims 1,3 ---	1-11
A	US 2001/044486 A1 (WESCH KARL) 22 November 2001 (2001-11-22) claims 1,2,7 ---	1-11
A	GB 1 341 623 A (DEGUSSA) 25 December 1973 (1973-12-25) column 1, line 20 ---	1-11
A	US 4 060 508 A (SUGAHARA YUJIRO ET AL) 29 November 1977 (1977-11-29) claims 1,9,17,29 ---	1-11
A	US 3 291 629 A (MAGNE FRANK C ET AL) 13 December 1966 (1966-12-13) claim 1 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/BR 92/00176

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 934689	A	21-08-1963	DE 1295820 B FR 1254722 A US 3377304 A	22-05-1969 24-02-1961 09-04-1968
US 2964484	A	13-12-1960	BE 560432 A FR 1186294 A GB 861971 A GB 877133 A GB 877136 A GB 877135 A NL 110976 C NL 220398 A NL 302893 A NL 302894 A US 3042692 A US 3006936 A US 3035069 A	19-08-1959 01-03-1961 13-09-1961 13-09-1961 03-07-1962 31-10-1961 15-05-1962
EP 0337237	A	18-10-1989	DE 3812014 A1 BR 8901687 A EP 0337237 A1 JP 1311151 A	26-10-1989 21-11-1989 18-10-1989 15-12-1989
DE 3839418	A	08-06-1989	DE 3839418 A1 FR 2623514 A1 GB 2212808 A , B IT 1227542 B JP 1168747 A	08-06-1989 26-05-1989 02-08-1989 15-04-1991 04-07-1989
US 1538861	A	19-05-1925	NONE	
US 1357876	A	02-11-1920	NONE	
US 2001044486	A1	22-11-2001	DE 19509085 A1 AT 231174 T BR 9607664 A CA 2215675 A1 DE 59610056 D1 WO 9628505 A1 EP 0815167 A1 JP 11502240 T ZA 9602143 A	19-09-1996 15-02-2003 16-06-1998 19-09-1996 20-02-2003 19-09-1996 07-01-1998 23-02-1999 16-09-1996
GB 1341623	A	25-12-1973	DE 2009047 A1 AT 305962 B BE 763422 A1 CA 933938 A1 CH 567009 A5 FR 2079133 A5 NL 7100320 A , B,	02-09-1971 26-03-1973 24-08-1971 18-09-1973 30-09-1975 05-11-1971 30-08-1971
US 4060508	A	29-11-1977	JP 1106397 C JP 51057749 A JP 52032899 B DE 2551220 A1 FR 2291246 A1 GB 1504999 A NL 7513344 A	30-07-1982 20-05-1976 24-08-1977 15-07-1976 11-06-1976 22-03-1978 18-05-1976

Information on patent family members

PCT/BR-02/00176

Form PCT/ISA/210 (patent family annex) (July 1992)